ELECTROCRYSTALLIZATION OF METALLIC THIN FILMS ON DIFFERENT SUBSTRATES: EFFECT OF OPERATING PARAMETERS

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE

REQUIREMENTS FOR THE DEGREE

OF

MASTER OF TECHNOLOGY

IN

METALLURGICAL & MATERIALS ENGINEERING

SUBMITTED BY

Kheer Sagar Maitry

Roll No: **212MM1417**

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

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CERTIFICATE

This is to certify that the thesis entitled, **"Electrocrystallization of metallic thin films on different substrates: Effect of operating parameters"** submitted by Kheer Sagar Maitry in partial fulfillment of the requirements for the award of Master of Technology in Metallurgical & Materials Engineering from National Institute of Technology, Rourkela is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree.

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Date 22/05/2014 Kheer Sagar Maitry

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Abstract

Thin films are two dimensional layers with a thickness usually in the order of nanometers to microns, which is negligible when compared to the bulk of a material. Thin films play a vital role in many prospective fields like energy, mechanical and metallurgical solutions. The current work focuses on the grain growth, crystallinity and induced stress in copper thin films synthesized by electrodeposition on graphite and stainless steel (SS) substrates.

Cu thin film deposition was carried out (i) at a constant voltage (0.35V) with varying temperature of deposition and (ii) at constant (room) temperature with varying voltage for each substrate. The nucleation and grain growth behavior of Cu on Graphite was studied by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Induced stress of the film was calculated from Stoney formula from the surface profilometer data.

It was observed that in case of fixed voltage tests, low temperature (10°C) was not favorable for the grain growth and higher grain growth was observed with increase in bath temperature (18 & 20°C). Similarly, for fixed temperature tests, higher deposition voltage (1.3V) resulted in high nucleation rate and grain growth than low voltage values (0.7 & 1.0 V). XRD analysis revealed that crystallinity of the Cu film was much better in case of graphite substrate compared to SS substrate. It may be due to the favorable crystal structure of the SS substrate. Stress condition obtained by profilometer tests revealed the trend of varying stress condition based on the temperature and substrate. Tensile stress condition is detrimental for thin film as compressive nature prevents cracking.

Keywords: Thin films, Electrodeposition, Copper, Nucleation, Grain growth, SFM, Surface profilometry, Surface analysis.

CHAPTER 1

INTRODUCTION

Introduction

Research motivation

Objective

1. INTRODUCTION

1.1 Introduction

Electrochemical metal deposition is an attractive technique when compared to other vapor deposition methods like CVD (Chemical vapor deposition) and PVD (physical vapor deposition) as large scale coatings for various applications are possible by this technique. Electro- deposition is normally associated with a growth process where the nuclei formed on the electrode surface are highly dependent on the applied voltage. This technique offers various advantages, e.g. low processing temperatures, a large number of pure metal and alloys can be electrodeposited, easy to control (by customizing the electrodeposition parameters), deposits easily onto complex shapes, control of film thickness carried at low cost which is difficult by any other traditional processes [1-5]. Origin of electrodeposition of metals started since 19th century and galvanic cells were used as sources of direct current. In electrodeposition process, metal deposition takes place at electrode/electrolyte interfaces under the influence of applied potential and these take with a number of phase formation phenomena. Technological importance of electroplating are of greater interest and used for production of different functional coatings and decorative.

The electrodeposition of copper on various substrates enables high quality interconnects in IC fabrications, printed-circuit boards and hard disc read heads, also for protective coatings on any conducting substrate. Copper electrodeposition is a simplest technique and possesses high industrial importance to obtain inexpensive copper thin films which are employed in the semiconductor industries due to its better conductivity. Copper electrodeposition has been studied on numerous substrates [6 -11]. Cu has been widely used for magnetic applications [12] and remains one of the cheapest available substrate in electrochemistry. Graphite is the most commonly used supporting electrode and frequently used graphitic electrodes are glass carbon, Highly Ordered Pyrolytic Graphite (HOPG) and graphite rods [13]. Their high inertness and low cost makes them a suitable candidate as the supporting electrode in electrodeposition technique [14]. Copper electrodeposition mechanisms are studied in both acidic and basic medium with and without complexing agent [15, 16]

Thin films have created an immense interest in renewable research applications. A thin two dimensional layer over a substrate results in decreased distance and it can induce new surface interaction phenomena. The decreased distance is more effective when compared to the bulk materials interaction. Their interactions are atomistic and helps in revealing many physical behaviors. However the physical properties of the films like electrical resistivity do not substantially differ from the properties of the bulk material and most importantly, thin film fabrication reduces the material waste and cost that usually happens in conventional bulk material device fabrication techniques. In general, thin films can be defined as a 2D layer, whose thickness ranges from nanometer to several micrometers. Thin films are used in fabrication of optoelectronic devices, photovoltaic, integrated circuits, tribology applications etc. Thin film property varies with respect to the thickness. Hence, thickness parameter relies basically on the application which we implement. They can be deposited in mass production-coatings methods like physical or by chemical deposition routes such as PVD, CVD and by electrochemical routes.

Growth of the film during the service of the device is one of the major factor which affect their accuracy and gained attention for usage to improve various properties (it may be electrical, magnetic, optical, mechanical properties) which results in increase of efficiency of the devices .e.g. grain growth of the films can cause a decrease in resistivity, hardness and the strength of the material. Intent study of deposition structure, growth and properties in a detailed manner is essential in order to obtain thin films of desired structure and stoichiometry and then be able to predict the optimal conditions for a particular deposition technique [17]. Thin films are mainly for the microelectronic devices, solar cells, magnetic devices etc.

The basic insight research on metal electrocrystallization was initiated by Max Volmer and his school during the 1920's [18-20]. Electrocrystalization is related to the problems of nucleation and crystal growth in a direct manner. In fundamental research of surface science, monitoring of the growth and topography of a metal deposited on a foreign substrate is invariably a challenge for fundamental research always which result is essential for many application fields. The starting initial stage of the growth process is frequently supported by the nucleation models which are related to the deposition method used. As a result of grain

growth in thin films, stress becomes tensile. A stable theory on crystallization kinetics was made by Avrami [21], in which the collision and overlapping of atoms leads to the multiple nucleation and grain growth. As nucleation is an important process in metal deposition, in one hand, the competition between growth and nucleation determines the granularity of the deposit. In one line it says that higher the rate of nucleation during deposition, the finer are the crystal grains of the deposit. The tradeoff between the nucleation and grain growth decides the morphology of the thin film. The nucleation rate controls the crystal grain size. Other influential parameters for varying the grain size are pH, buffer, complexing agent, deposition voltage and adding suitable supporting electrolyte to enhance conductivity of the bath composition.

1.2 Research Motivation

At present study of low temperature electrodeposition process is of greater interest to the scientist. This is convincing, has been successful and ambiguous in many respects. Most of the literature studies show less attention to the mechanism behind the electrochemical crystallization, more interest to morphological and structural investigations. The reliability is affected by the growth of the thin film and affects their electrical, mechanical, magnetic and optical properties. The present work has been carried with an aim to investigate the grain growth behavior in the electrodeposited samples on different suitable substrate. The samples have been prepared at different temperatures. Complete analysis would allow investigating the impact of nucleation, growth and different parameters (thermodynamics and kinetics) on deposition mechanism, and structure and properties of the thin film deposits. Above points are the key objectives of the current study. It extends the work to the nucleation and growth mechanisms at different low deposition temperatures. Low temperatures accounts for the effects of decreased surface roughness, change in grain habitat with a greater extension to better deposit/substrate interface properties. This low temperature factor is something which was less investigated before.

1.3 Objective

The objectives of the present study are:

1. Electrocrystallization of copper on graphite and ferritic stainless steel substrates.
2. Study the effects of various temperatures and potential on morphology of copper deposits.
3. Characterization of the fabricated films by XRD, FESEM and Stylus Surface profiler.
4. Comparison of the structural features.

CHAPTER 2

LITERATURE REVIEW

Thin film Technology

Synthesis of Thin films

Electrodeposition Technique

Nucleation and Growth Mechanism

Factors affecting nucleation and growth

2. LITERATURE REVIEW

2.1 Thin Films Technology

Thin film is a solid material when grown as a thin layer (nano-micrometer range) on a solid substrate by controlled condensation of the individual atomic, molecular, or ionic species by physical process or chemical reactions. Any variety like organic, inorganic or a metallic coating (deposition) can be done depending on the type of application. It not only expands the life of the surface but also protect the surface from different environmental attacks. Thin film deposition technique is regarded as an economically feasible technique.

Many materials are reactive either to chemicals or light leading to corrosion. Hence it is necessary to protect such kind of materials by protective coatings. Miniaturization of components increases the surface to volume ratio of the involved materials. Hence advanced materials gains more importance on interface engineering and surface properties. Hence by surface coatings, the properties such as wear, friction and corrosion based troublesome parameters can be neglected to a certain extent by such thin film coatings. Change in dimension results in changing the physical property of the material itself. High application coatings techniques need extremely costly equipment's for deposition (PVD, CVD) which are not a suitable solution for large scale production. Preferably, electrodeposition gains attention due to its ease and its ability to utilize for large mass production made it a better candidate for vast engineering applications.

High crystalline deposits can be obtained by electrodeposition. In case of complex surfaces, other conventional techniques could not do the job properly as electrodeposition does. Electrodeposition also plays a vital role in semiconducting industries. Their excellent stability and accuracy have made them a convenient method in the semiconductor device industries.

A brief chronology of progress of thin film technology is as follows: observation of interference patterns (e.g. oil on water) observed by R. Boyle et al. (~1650). In the year of 1850, M. Faraday et al. have analyzed the development of first deposition techniques and in the same year a brief research on determination of thickness by Arago, et al. with a commercial introduction of electrochemistry (Galvanic) for gold plating. Manufacturing

(industrially) of different coating materials for optical, electronical and mechanical applications in the year ~1940. In semiconductor and optical industry, technology develops to mass manufacturing processes in ~1965. Thin films of high T_c superconductors are produced in the year ~1990. After five years (~1995) improvements on atomic and nanoscale, variations were proven to be successfully carried. Nanocrystalline materials with defined composition and structure can also but used for manufacturing of protective coatings application. Highly ordered 2D and 3D objects deposition (in the nm range) and up scaling of complex reactive coating processes like thermal management and coatings on glass (~2000) was also initiated. Recently, investigation of organic coatings in came into picture (~2006).

2.1.1 Film Deposition and Film Formation

Three phases involves in the thin film deposition:

1. Suitable precursors for the supply of ions (atoms, molecules, cluster)
2. Transport of the ions from the source to the substrate
3. Particle adsorption after reduction leading to nucleation and grain growth.

Since all these parameters are highly controllable in electrodeposition technique, they are highly flexible and yields better throughput than the other deposition techniques.

2.2. Synthesis of Thin Films

2.2.1 Physical Deposition

Physical method covers the deposition techniques which basically depend on the evaporation or ejection of the material from a source. Structure/property relationships are the basis features of thin film technologies. Underlying the performance and economics of thin film, components are manufactured by manufacturing techniques on a specific chemical reaction. Hence chemical reactions depends on thermal effects (e.g. in vapor phase deposition) and thermal growth.

However, in all these cases a specific type of chemical reaction is essential to attain the final film. Physical method explores the deposition technique which depends on the evaporation or ejection of the material from a source, whereas chemical methods depend on physical properties. Alternative is the formation of this film from the precursor materials (e.g. gaseous

iodization, sputtering ion beam implantation, thermal growth, CVD, MOCVD and vacuum evaporation). Also certain techniques which are only capable of producing thick films include screen printing, glazing etc.

2.2.2 Chemical Deposition

Owing to the versatility for the deposition of large no of elements and compound at low temperature, Chemical deposition is an important method for deposition of thin film. Chemical deposition can be defined as a material synthesis process in which the constituents react together to form a solid film at surface. Chemical reactions are the essential characteristic of this method. It is required to understand reactions of the reactants rather than controlling the usual deposition process variables or parameters. Various types of chemical reactions are employed in CVD process for the solid film depositions are mostly pyrolysis, reduction, oxidation, hydrolysis, synthetic chemical transport reaction etc.

This deposition process has been economically effective as well as industrially exploited at a large scale. It may be a Gas phase e.g. Chemical Vapour Deposition (CVD), Plasma Enhanced CVD (when a plasma is used to induce or enhance decomposition and reaction), Metal Organo CVD (MOCVD) (metal-organic species are used as precursors), Laser CVD, Photo CVD, Atmospheric Pressure CVD etc or Liquid phase deposition (Electro Deposition, Electroless Deposition, Spray Pyrolysis, Sol Gel Process, Solution Growth Technique, Anodization, Liquid Phase Epitaxy (used to deposit single crystal films) process). Chemical vapour deposition (CVD) processes are extensively used in industrial application results from the versatility of depositing a variety of compounds with perfection and purity covering a range from amorphous deposits to epitaxial layers. CVD techniques are extensively used for deposition of protective coating for a variety of environmental attacks; protection is required against wear, erosion, and high temperature oxidation [22]. Liquid phase chemical deposition process is regarded as growth of inorganic film from liquid phases accomplished primarily by electrochemical processes and by chemical deposition process plating, conversion etc. Number of profound reviews explored different processes of the film formation with their theory and practice [23] [24-26].

2.3 Electrodeposition Technique

Electrochemical deposition is a process involving the synthesis of films from dissolved species results from the change in their oxidation states by the use of electricity. Metal deposited at electrode within an electrolyte junctions under the influence of electric field. It can easily be fabricated over pure metals as well as compounds like phosphides and oxides. When chemical changes occur due to passage of electric current through an electrolyte is termed as electrolysis and substance deposits on an electrode surface as consequence of above process is known as electrodeposition. Main applications are observed in the electronics industries, which interconnects the deposition of Cu in integrated circuits and the on magnetic materials. The application field contains a section of phenomena (e.g. corrosion and electrophoresis), technologies like electroplating of metals and aluminum production, devices such as elctrochromical displays, batteries, fuel cells, and analytical sensors. Three electrodes system (contains a working electrode, a counter and a reference electrode) is generally used in Electrodeposition. Metal deposition occur on a substrate, taken as a working electrode, platinum electrode or graphite rod with 0.2 cm diameter, as counter and saturated Calomel Electrodes as reference electrodes. The bath temperatures are maintained at ambient as well as sub-ambient temperature for the different deposition potentials. Deposition technology, involves in the reduction of ions ($M_{sol}^{z+} + Ze \rightarrow M_{lattice.}$) from organic, aqueous and fused salt electrolysis by reduction due to the externally applied voltage.

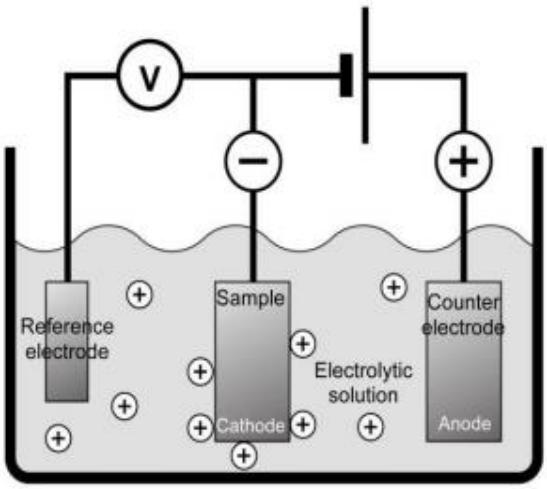


Fig. 2.1: Schematic representation of a standard three electrode cell.

In a three electrode system, all the electrodes are immersed in the electrolyte contacting the precursor ions for the deposition. The four major aspects taking place in any electrodeposition techniques are given below:

I. Electrode-electrolyte interface
II. Kinetics and thermodynamics
III. Nucleation and growth mechanism
IV. Structure and properties of the deposits [27-29].

2.4 Nucleation and Growth Mechanism

Analysis of nucleation and growth mechanism of electrocrystallization has significant interest because of its application in metal thin film production for different fabrication process of alloys, nano-particles with high degree of precision.

A general theory on multiple nucleation and growth in the case of electrocrystalization was emphasized by Fleischmann and Thirsk [30] (1960). Armstrong and Harrison in the same year [31, 32] expanded the above theory both considering the process of electrochemical multinuclear and multilayer growth. A theoretical and experimental study on electrocrystallization of metals by Bockris, Damjanovic and Despic [33–34], gave contributions about problems relating surface diffusion, propagation and bunching of steps and dendritic growth. The investigated of substrate, nucleation and grain growth on texture development was studied in brief by Epelboin, Froment et al. [35, 36]. They explained by characterization techniques like XRD and SEM.

Butler-Volmer equation signifies the current density on a metal substrate as function of overvoltage. In a homogeneous surface, the current density can be distributed evenly throughout the surface. A foreign atom to deposit on a substrate requires a new phase in the first step of electrodeposition. Further deposition is kinetically limited by the Gibbs formation energy, which is dependent on the cluster size of the new phase formed, where N = number of atoms forming the cluster. The Gibbs formation energy of a cluster of N atoms is given by:

$$\Delta G(N) = -Nze|\eta| + \Phi(N) \quad \text{---------- (1)}$$

The negative term resembles the N-number of ions transferred from the electrolyte of the bath solution to the substrate under the influence of voltage and the positive term represents an excess free energy considering energy contributions obtained from the deviation of the new phase from the initial phase. The location where a film meets the substrate surface is called an interface. Films and Interface formation commence on a substrate surface. The first indication of the film to form is called a nucleus and the process by which nuclei of a new phase form is called nucleation. The transformation occurs in two steps:

Step 1: The formation of tiny stable particle is called Nucleation.

Step 2: The increase in size of these stable particle called Growth.

The formation of nuclei of a new phase (e.g. a solid particle of phase B in a gas vapor phase A) presented in equation form [$A_{(g)} \rightarrow B_{(S)}$]. For a new surface to form in the process of nucleation the most often observed process are those that minimize the required energy. The reactants and reaction conditions (concentration, temperature and pressure etc.) could possibly render the reaction to form $B_{(s)}$ in $A_{(g)}$ at ($-\Delta G_{reaction}$).

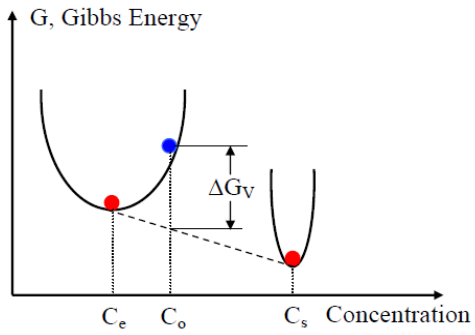


Fig. 2.2: Schematic of variation of overall Gibbs free energy of a supersaturated solution followed by solid phase formation with balanced equilibrium.

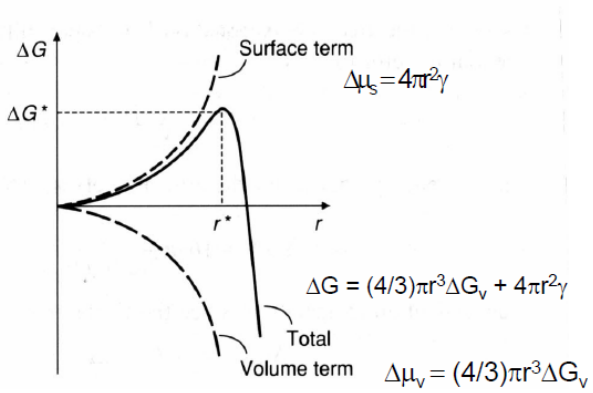


Fig.2.3: Schematically shows the nuclei radius change with respect to volume free energy, Δμv, surface free energy, Δμs, and total free energy, ΔG.

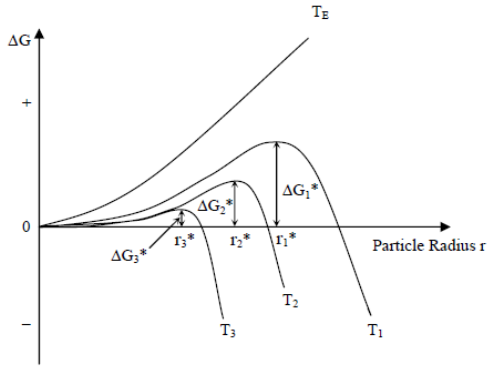


Fig.2.4: Comparison of the critical sizes, critical free energy of three spherical nuclei with supersaturation, which increases with a decreasing temperature.

2.4.1 Electrode Solution Interface

When two dissimilar phases come into contact, charge separation occurs in the interfacial region between an electrode and an electrolyte. As almost all surfaces have an excess electric charge. In general it results in an interfacial potential difference or electric field. The double layer region describes the arrangement of charges and dipoles alignment at the interface. The double layer at the interface has electrical, compositional, and structural characteristics. Electro-neutrality is valid in bulk solution, as forces experienced by ions and solvent molecules in this region are isotropic, no net alignment of solvent dipoles, and positive and negative ions are equally distributed throughout). And of course electro neutrality breaks down in surface region, as there is no net orientation of solvent dipoles in surface region and forces experienced by ions and solvent dipoles are no longer isotropic and homogeneous.

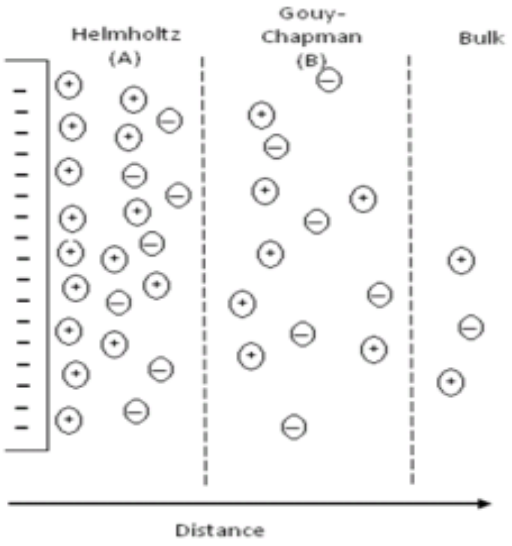


Fig.2.5: Showing double layer at electrode/solution interface.

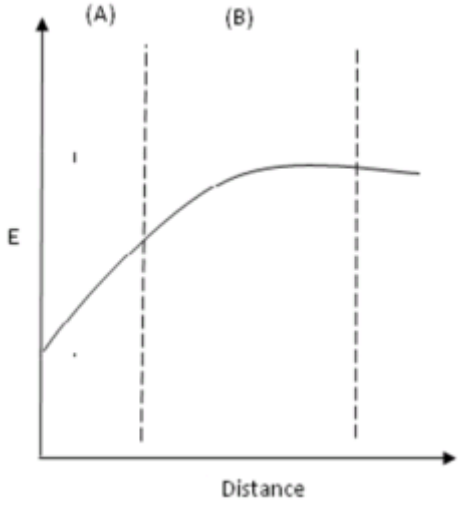


Fig.2.6: Potential distribution across distance.

Figure shows the distribution of anions and cations at the interface region and potential varies linearly. Transport processes at an electrochemical interface are schematically represented below:

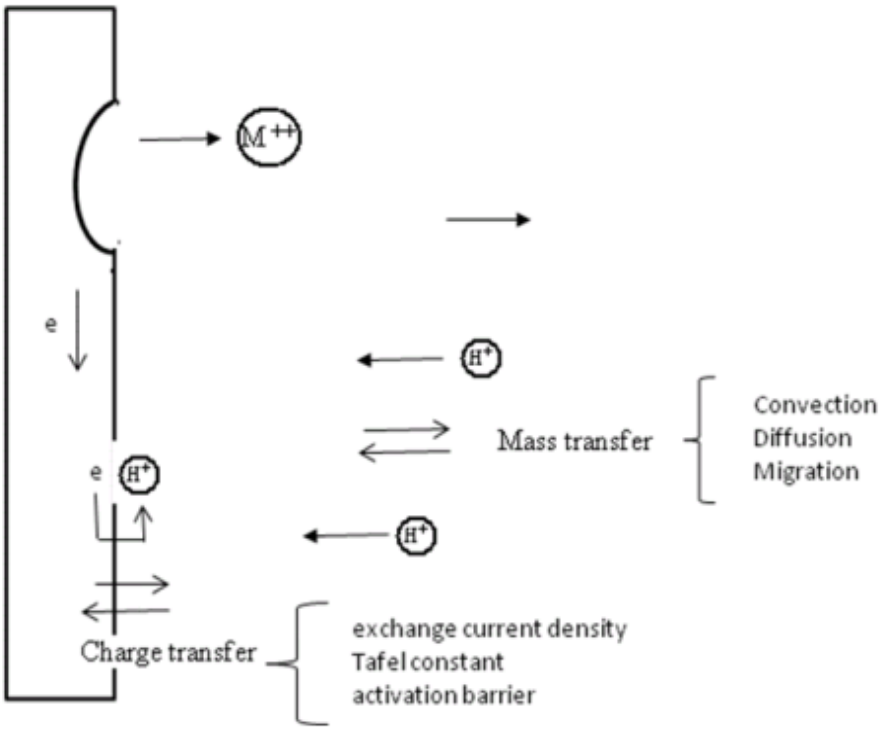


Fig.2.7: Transport processes at electrochemical interface.

In electrochemistry, the charge transfer has contributed in the solvent which results in the metal deposit. This charge transfer takes place in both aqueous and non-aqueous medium. Unlike non-polar medium, a potential drop at the interface occurs in polar solvent such as methanol, water. A model on double layer was proposed by Bockris, Devanathan, and Muller by taking account of these parameters.

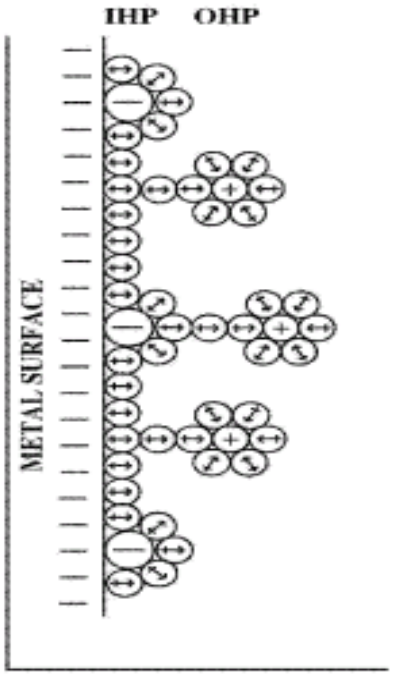


Fig.2.8: Water dipole model of the double layer at an electrode/electrolyte interface

A strong interaction between the charged electrode and the water dipoles results in the formation of water molecule layers attached to the substrate. The adsorbed ions presents along the substrate layer takes part in inner Helmholtz layer (IHL) and the hydrated ions will contribute to the formation of outer Helmholtz layer (OHL). Next to OHL, the diffusion layer is present. During deposition, the ions which permeate through the diffusion layer will undergo reduction reaction for the thin film formation. The double layer region is influenced by various parameters like electric field, *pH* and ion concentration and conductivity of the bath composition etc.

2.4.2 Thermodynamics and Kinetics of Deposition Mechanism

The ions attracted to the cathode of the perfect crystalline material possess less binding energy. The ions initially stick as adions on the substrate surface. The arrival of new ions results in the formation of nucleation sites. The adions adsorbed on the substrate are usually thermodynamically unstable and the stability is achieved by nucleation. Ions concentration, temperature and the bath composition conductivity plays a significant role in nucleation and result in cluster formation.

At state of thermodynamic equilibrium, the electrochemical system is stable comprising of metal ions in solution, metal adatoms on an electrode and metal atoms in the deposit. This situation is not favorable for formation and growth of a phase. Favorable conditions for a first order phase transition occur when the solution is supersaturated [37, 39]. Defect density is an important parameter, as it is taken in to account to observe quantitatively the speed of grain growth within the as-deposited grains. Supersaturated solution will provide a favorable situation for the initial phase formation [38]. The defect density is an important parameter, as it is taken in account to observe quantitatively the speed of growth within the as-deposited grains. ‘‘Self-annealing’’ has been remarked in electroplated Cu films stored at room temperature [40–46].The electrodeposition kinetics are hard to study. Although the self-annealing behavior of electroplated Cu is interesting, the main reason behind this is the grain structure and impurity content of the film. Room-temperature self-annealing has not been widely observed in vapor deposited Cu. By varying the temperature, it is possible to determine activation energy [47, 48, 49].

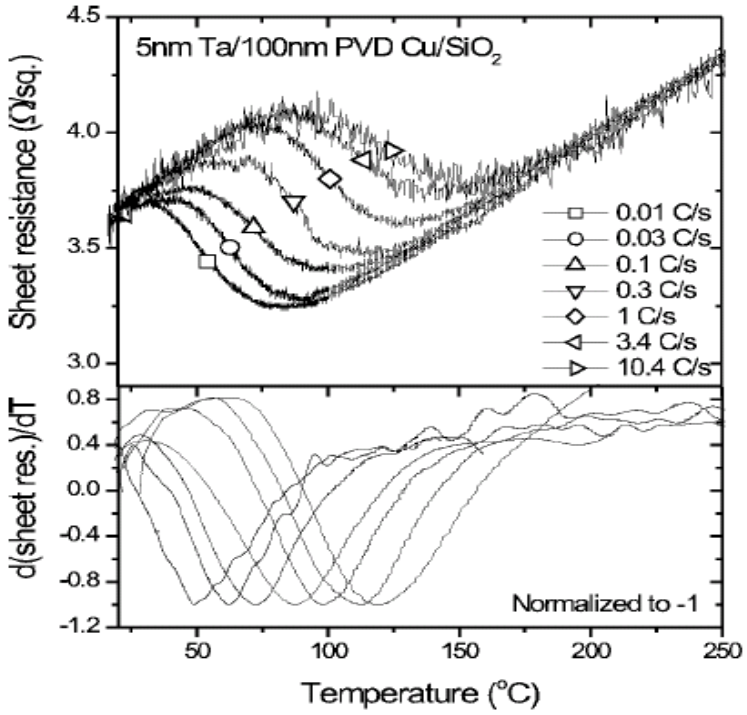


Fig.2.9: In situ sheet resistance vs annealing temperature for 100 nm films sputtered onto SiO2 and capped with a 5 nm Ta layer. The rate at which the temperature of the sample was increased is indicated [50].

In Figure 2.9, a drastic reduction in resistance indicated the microstructuralral change in the Cu film. If resistance decreases, and shifted to a higher temperature for higher ramp rates, it indicates microstructural change is thermally activated. This decrease in resistance causes the mean-free path of the electrons to increase. Kissinger analysis was performed to study the kinetics.

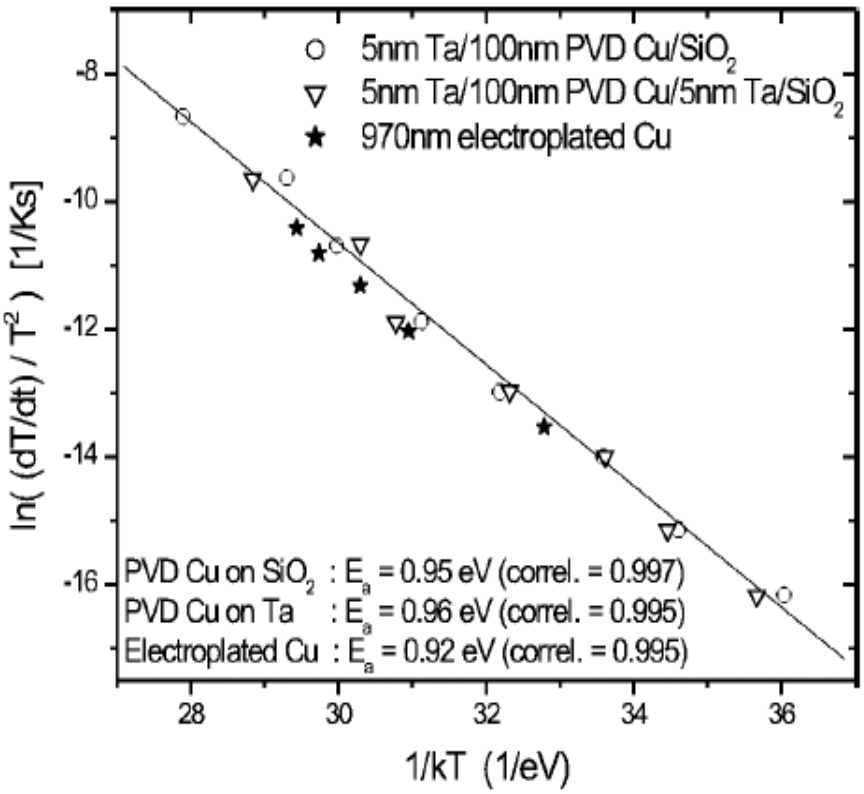


Fig.2.10: Kissinger-type analysis of the sheet-resistance data measured during annealing treatments at different ramp rates. The samples are 100 nm sputter deposited films on SiO_2 substrates ~ with and without 5 nm Ta interlayer And 970 nm electroplated films [50].

2.5 Factors Affecting Nucleation and Growth of Thin Films During Electrodeposition

As shown in figure 2.11 several factors affecting the nucleation and growth of deposits as a bath composition, temperature, reaction potentials, agitation of the electrolyte etc. Details of these are explained separately.

2.5.1 Effect of Temperature

Increase in the temperature of electrolyte bath the diffusion of metal ions within the electrolyte increases according to the equation $D = D_0 exp^{-Q/RT}$. Therefore a decrease in the

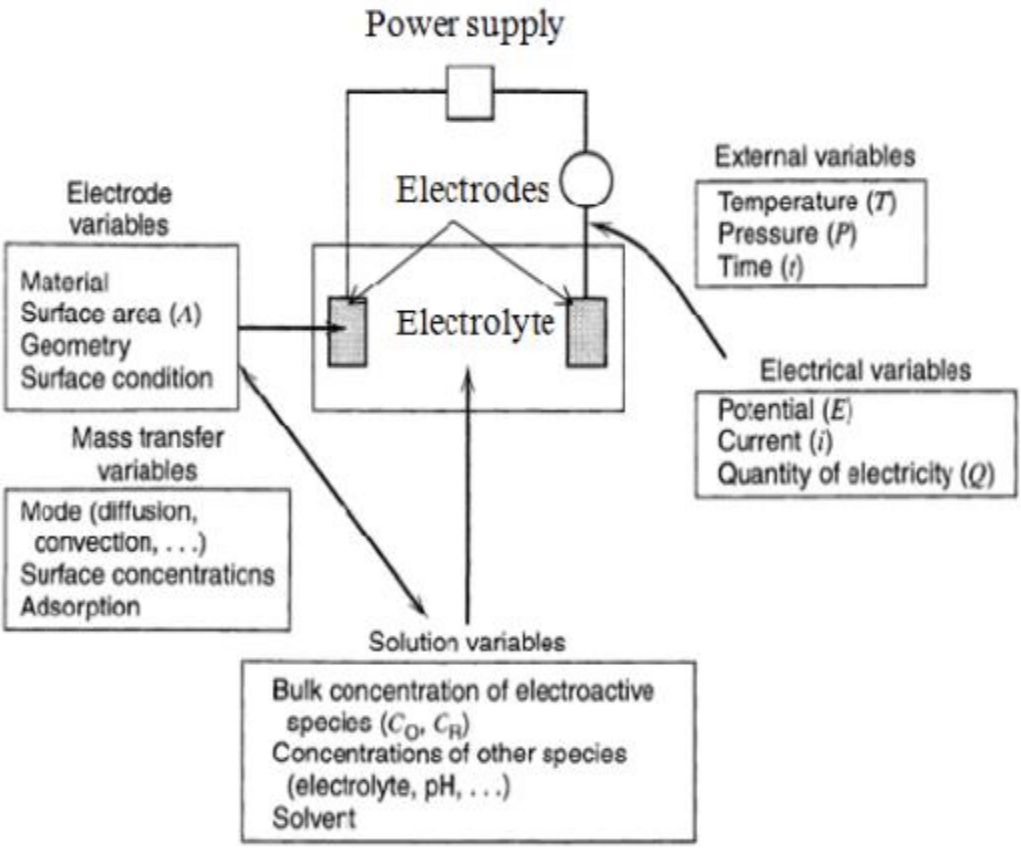


Fig.2.11: Variables affecting electrochemical phase formation.

cathode over potentials, ions source moves toward the cathode increase with the effect of increasing temperature, heat, an another form of energy due to this energy of nucleation increases. It is indicated that for these increased energy of nucleation rate of nuclei formation decreased and observed preferred growth of nuclei causing formation of large grains [51-54].

2.5.2 Effect of Acid Concentration

Formation of preferred smooth bright deposits at lower concentrations used to study the variation in the surface morphology with acid concentration. Still medium concentration tends to improve the nucleation rate. When the concentration is increased the hardness value also in the same manner is declined. Electrode potential shifts toward more positive and negative values with increase in acidic concentrations within the cathodic (positive) and anodic (negative) range. Increasing alkalinity of the solution, i.e. above 8.5 results in decrease in the cathodic efficiency [55]. Metal deposit in open circuit potential turns into more

negative value as the concentration of acidic solution increases, it does not vary with time and also depends on the concentration value of the solution, (i.e. H+ ions). When the acid concentration of electrolyte is decreased it tends to increase the hydrogen evolution. Bubbles of hydrogen get clasp on the surface and effective surface area of the metal reduction reaction decrease. A decrease in bulk concentration because of high polarization results the decrease in crystallinity and grain size of deposition [56].

2.5.3 Effect of Copper Concentration

Easier thin films formation occurs when the concentration of copper is high in the bath. Increase in Cu concentration causes the rate of nucleation and growth to be increased. Coarsening of grains is observed when the current density of deposits is much higher, mostly spongy and dark grains are formed. Research review also tells the formation of fresh nuclei is feasible only when the concentration of copper has to be increase in the electrolyte bath. By analyzing certain experimental study information reveals that increasing concentration, the rate of formation of nuclei is really decreased. The main upgrading in the deposit is due to increase in the rate of growth of crystals above cathode surface [57]. To acquire thin film of different metals this technique frequently applied for enough thickness, structure and adhesion [58]. The metal surface influenced by the nature of thin film deposit [59] and properties of thick metal deposit largely affected by the bath composition and condition [60].

CHAPTER 3

EXPERIMENTATION

Experimental Setup

Electrolytic bath Preparation

Substrate Preparation

Synthesis

Electrochemical Analysis

Characterization Technique

3. EXPERIMENTATION

3.1 Experimental Setup

A potentiostat consists of either a three or two electrode system which comprises of working, counter and reference electrodes. The reference electrode is used to find the potential drop taking place close to the working electrode and the solution interface. Hence the exact potential required for the deposition of any thin film can be determined by a standard three electrode system. The working electrode is the cathode (negative) on which the desired thin film is deposited. An inert electrode (positive) such as platinum or graphite is used to provide sufficient electric filed during electrodeposition. The area of the working electrode should not be in excess which may lead to potential instability. Also, inertness of counter electrode is most important. During the redox reaction, they should not involve in any reactions. The most commonly used counter electrodes are platinum in mesh or rod form and graphite electrodes.

All electrodes are connected to Poteniostat-Galvanostat (Eco Chemie Netherland, Autolab PGSTAT 12) system having computer interface of GPES software. Electrochemical experiments are controlled with a potentiostat-galvanostat under a computerized control. The deposition is performed at ambient and sub ambient temperature under a magnetic stirring using a two electrode system.

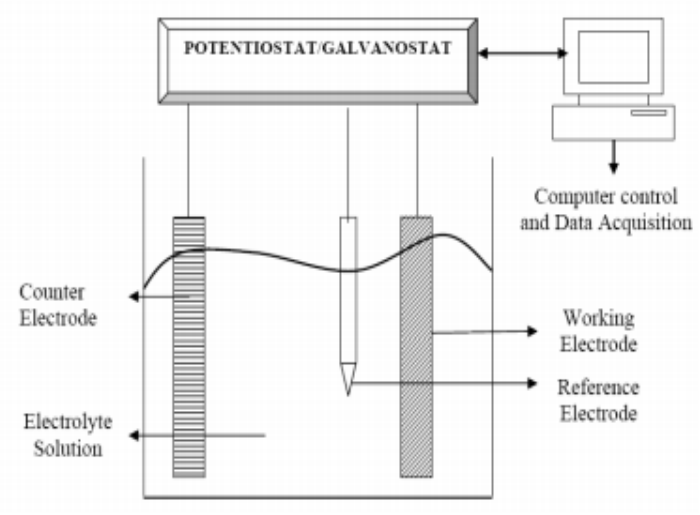


Fig. 3.1: Experimental setup of Potentiostat/Galvanostatwith standard three electrode cell.

3.2 Electrolyte Bath Preparation

Electrolytes containing 0.1M of Copper (II) sulfatepentahydrate ($CuSO_4.5H_2O$) were prepared using reagent grade chemicals. Solution was adjusted by adding diluted reagent grade 98% pure 40 g/l of sulfuric acid (H_2SO_4) and 1 M Sodium sulphate (Na_2SO_4). The purpose of using conc. H_2SO_4 is to make the solution electrically conductive. All solutions were prepared using double distilled water from Distillation Unit. All chemicals were from commercial sources and highest purity available. They were used without further purification.

Different bath compositions for copper deposition were performed. 0.1M of Copper (II) sulfatepentahydrate ($CuSO_4.5H_2O$) was prepared using reagent grade chemical. Solution was adjusted by adding diluted reagent grade 40 g/l of sulfuric acid (H_2SO_4). These solutions were used to perform in graphite substrate at various potential.

Again 0.1M of Copper (II) sulfatepentahydrate ($CuSO_4.5H_2O$) was taken using reagent grade chemical. Solution was adjusted by adding dilute reagent grade 40 g/l of sulfuric acid (H_2SO_4) and added ethanol to solution for better deposition on stainless steel substrate so that we can perform at various potential.

3.3 Substrate Preparation

Graphite samples were cut from graphite sheet by using hacksaw blade. The samples were cleaned by using water and acetone/ethanol, and then samples were dried. On graphite, an area of $0.05cm^2$ was marked and carefully covered rest part with non-conducting tape.

Ferritic stainless steel samples were cut from stainless steel sheet by using sheet cutter or simple scissor. The samples were cleaned by water then dried it properly for polishing, after polishing with emery paper it was dipped in nitric acid for surface cleaning. Use cotton after cleaning from distilled water. On stainless steel an area of 0.05 cm^2 was marked and carefully covered rest of part with non-conducting tape.

3.4 Synthesis

Electrodeposition techniques were used for copper deposition and potentiostatic mode was employed for this. The working and counter electrodes were immersed in an electrolytic bath along with the reference electrode. The deposition was performed at -0.35 V potential with

Chronoamperometry method with different temperature of deposition. The temperatures were maintained at 10, 18 and 25^{o}C with graphite as the substrate. The depositions were also performed at different potential level at affixed temperature both on graphite and stainless steel substrate. The potential levels were -0.7, -1.0 and -1.3 V and the experiment set were done at ambient temperature and 15^{o}C.

3.5 Electrochemical Analysis

In the present work of phase transformation was analyzed by chronoamperometry method.

3.5.1Chronoamperometry

Chronoamperometry (CA) or Potentiostat transients are one of an electrochemical technique. The potential is stepped to the working electrode and the resulting current at the electrode during the potential step is monitored as a function of time. This current ~ time response is having two components, first is the current due to charging the double layer and second one is due to the electron transfer reaction with the electro active species. When the working electrode is dipped inside the electrolytic solution, a thin electrical double layer created at the electrode/electrolyte interface. The double layer involves distribution of ionic species at the interface. It is considered to be working as a capacitor (C) that represents the electrode double-layer capacitance [61]. Current flows in direction opposite to direction of flow of the electrons to the working electrode (WE) in order to obtain its potential to some chosen value. A potentiostat with a 3-electrode cell provides required current via the Auxiliary electrode (AE) to the Working Electrode. And at the same time the potential is measured with respect to a Hg/HgCl (RE). The Cottrell equation shows the current (I) decreases as a function of time (t) as shown in the figure [3.2]. The current decay is given by Cottrell law [63]:

$$i = \frac{nFAD^{1/2}C^{b}}{(\pi t)^{1/2}}$$

Where, n is the number of electron transferred per molecule or ion; F is the Faraday's constant; A is the area of the electrode surface in cm^2; D is the diffusion coefficient in cm^2/s; $C^b$is the concentration of the electro active species in mol/cm^3; t is time in second.

The current raises rapidly to a maximum value decays as a function of $t^{1/2}$ according to eqn. Several potential parameter were performed (-0.35 V, -0.7 V,-1.0 V and -1.3 V) on graphite and stainless steel substrate.

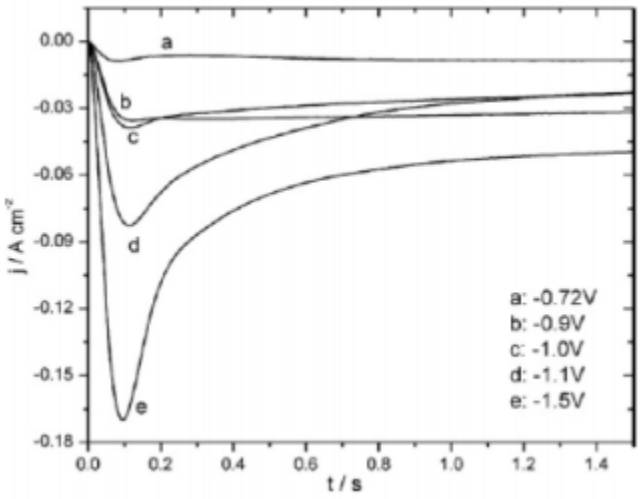


Fig. 3.2: Chronoamperometry (Current-time transient) Curve [63].

3.6 Characterization Techniques

Numerous techniques have been used to characterize the electrodeposits of copper thin films. Some details of the techniques are enlisted below. The technique utilized in this study includes XRD to investigate the phase, crystal size and lattice strain, Surface Profilometer to investigate the film thickness. The microstructure studies of the deposits were done by SEM. Energy dispersive spectroscopy (EDS) analysis was used to determine the chemical composition/purity of the deposited films.

3.6.1 X-Ray Diffraction (XRD)

X-ray diffraction is line profile analysis and is a versatile technique, powerful tool and nondestructive method through which behavior of different materials are analyzed. It gives information about the phase analysis, crystallographic structure, lattice parameter, interplanar spacing of any materials. XRD techniques were used to determine the crystallite size, lattice strain, crystallographic structure and desired orientation in polycrystalline or powered solid samples. The high intense scattered X-rays give the characteristic features of the materials.

Effect of the finite crystallite size was understood by peaks broadening.In the present study the scanning range angle was taken 40- 120^0 at a scan rate 3^0per minute with Cu K_α radiation where, λ=1.5406Å at an accelerating voltage of 30 kV, by using (PANalytical) Philips X' PERT System X-Ray Diffractometer.

3.6.2 Scanning Electron Microscope

Generally Scanning Electron Microscope (SEM) gives morphology and composition of samples which is obtained by JEOL 6480 LV scanning electron microscope (SEM) fitted with an energy dispersive X-ray detector of Oxford data reference system. Low acceleration voltage was in the range of 15 or 20 KV. The electron beam emitted from the electron gun performs a raster scan on the sample. The collection area and the number of electrons collected decide the pixels given in terms of resolution. During the scan, when the electron beam is incident on the sample several interactions takes place like elastic, inelastic, auger, radiative, non-radiative, X-ray generation, primary and secondary electrons generation takes place.

The emitted electrons are collected by the detector which is converted into image by the scintillation screen of the CCTV. The depth of penetration of the electrons depends on the conductive nature of the sample. The secondary electron emission takes place within 10 nm of the samples. Hence the surface features can be analyzed by Secondary electron mode. The elemental analysis is obtained from Energy dispersive X-ray spectroscopy (EDS or EDX).

3.6.3 Stylus Surface Profiler

The thickness of the thin film and residual stress components are determined by surface Profilometer studies. The analysis was carried out by the Dektak 150 surface Profilometer. The sample is mounted on the chuck. A Light is illuminated on the sample and the reflected light is directed towards the camera which is attached above the sample holder chuck. This inverted image obtained during the profiler scan is useful to fix the desired scan area. The profiler tip contains of a diamond tip whose radius ranges from 20 nm to 25 microns. The maximum resolution obtained for a 1 micron thick diamond tip is up to 1nm. The indentation force can be varied according to the nature of the samples. The tip force can be varied from 1 to 50 mg. The stylus radius used for the current measurement was 0.2 microns and the stylus force used was 0.3 mg. The scan length of 1000 microns was fixed for the scan. The tip

touches the sample and horizontally moves over the sample by scratching. The deflection of the tip is recorded by the sensors and the automation program enables to record a plot of scan distance and the height. The difference in height between the substrate and the thin film layer (Delta x) will give the thickness of the thin film. The radius of curvature of the substrate and the thin films are estimated and the residual stress analysis is performed by Stoney formula by the Dektak software. Other important parameters like roughness, 3D mapping and wear track depth etc. can also be analyzed using the profiler.

CHAPTER 4

RESULT AND DISCUSSION

XRD Analysis

Microscopic Analysis

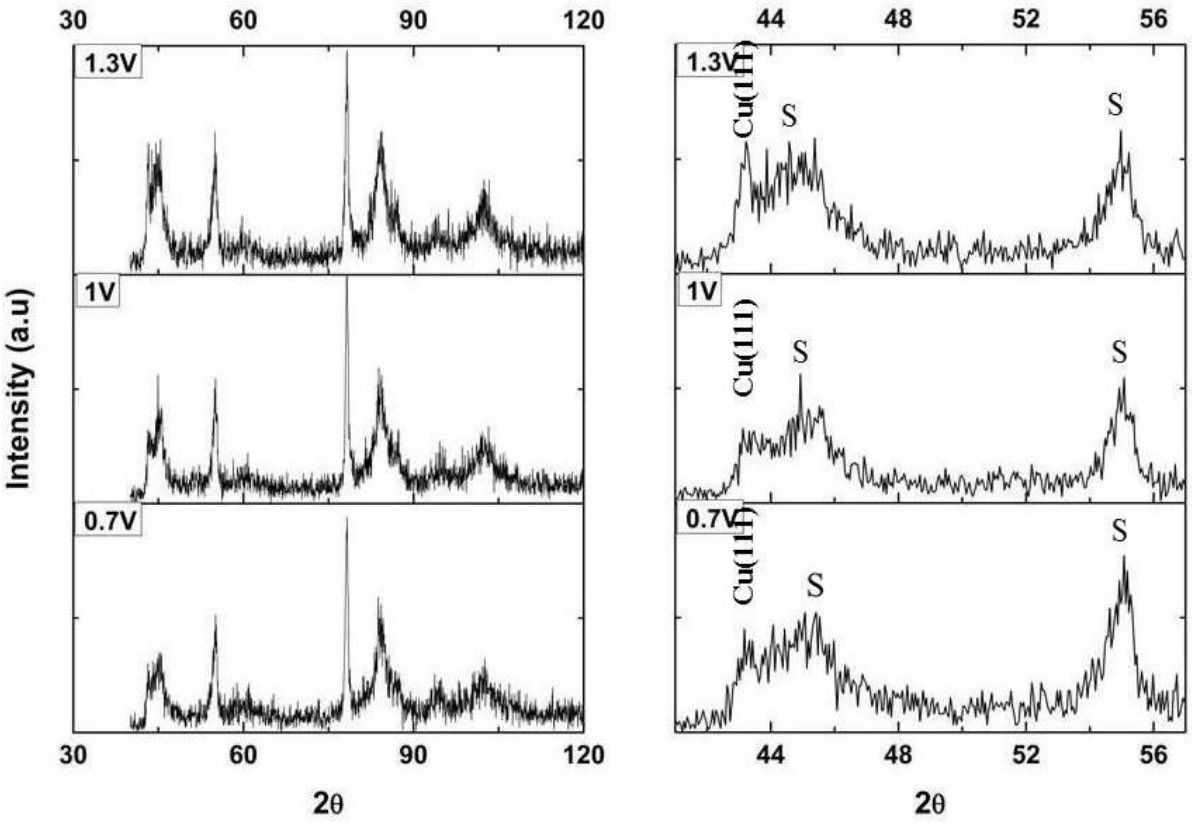
Stylus Surface Profiler Study

4. RESULT AND DISCUSSION

4.1. XRD Analysis

XRD patterns of the electrodeposited copper films have been illustrated in figures 4.1and 4.2.

Cu thin films at 25°C on graphite substrate

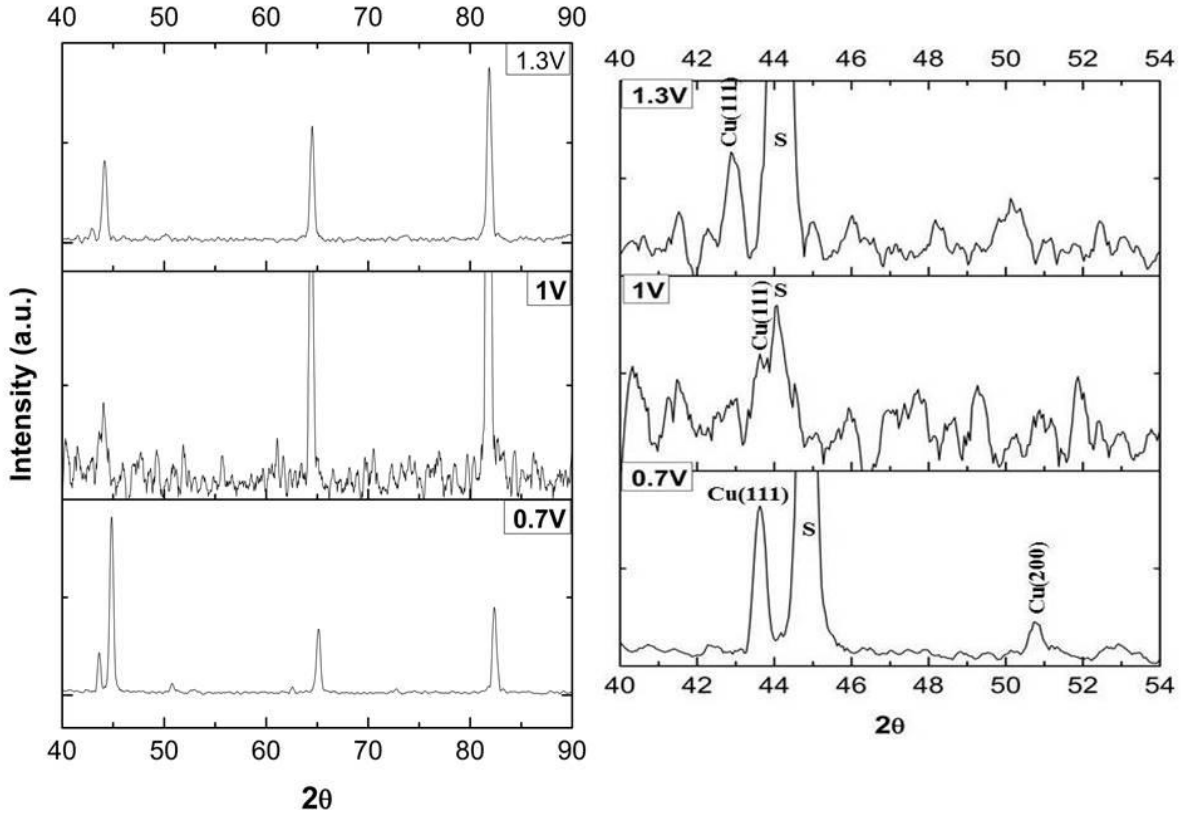


(a) (b)

Fig. 4.1: (a) XRD pattern of Cu thin films deposited on Graphite at 0.7, 1 and 1.3 V (25° C) (b) Expanded major peak.

Figure 4.1 shows the diffraction peaks of copper thin films deposited on graphite. 4.1(b) shows the expanded form of the major peak.From Fig. 4.1 it can clearly be observed that with increasing the potential value the peak intensity increases which may be due to nucleation and growth of more amount of Cu.

Cu thin films at 25°C on Stainless Steel



(a) (b)

Fig. 4.2: (a) XRD pattern of Cu thin films deposited on SS at 0.7, 1 and 1.3V (25°C)

(b) Expanded major peak.

Fig. 4.2 shows the X-ray diffraction peaks of Cu thin films on SS substrate. In case of low voltage deposition the intensity was prominent. The reason for this high crystalline nature may be due to the crystal structure of the substrate. The crystallinity in case of SS substrate is better than graphite as SS substrate helps in nucleation of FCC Cu. It can be noted that compared to other Vapor deposition techniques like CVD and PVD, the electrodeposited thin films usually yield better nucleation and growth. In the entire XRD plot some amount of peak broadening was observed and from those to calculate the crystallite size Scherrer Formula was used.

The formula is:

$$D = \frac{K\lambda}{\beta \mathrm{Cos}\,\theta}$$

Where, K is dimensionless shape factor its value close to unity, D is crystallite size of particles, λ is Cu $K_\alpha$radiation 1.5406Å and β is line broadeningFWHM (Full width half maxima) value.

Table 4.1 shows the calculated values of crystallite size of Cu deposits on both the substrates at different potential of deposition. The trend of these data is shown in Fig. 4.3. From the table and the plot it can be observed that in case of both the substrates, with increase in potential value (in negative) the crystallite size increases. This may be due to the higher growth rate at higher deposition potential. Peak broadening can also takes place due to lattice strain in the crystal; but in case of this type of aqueous process the strain amount is generally low.

Table 4.1: Crystallite size of copper deposits at ambient temperature (25°C).

Potential (V)	Substrate	Crystallite size (nm)
0.7	Graphite	14.5
1	Graphite	14.5
1.3	Graphite	28.9
0.7	SS	10.1
1	SS	10.9
1.3	SS	21.7

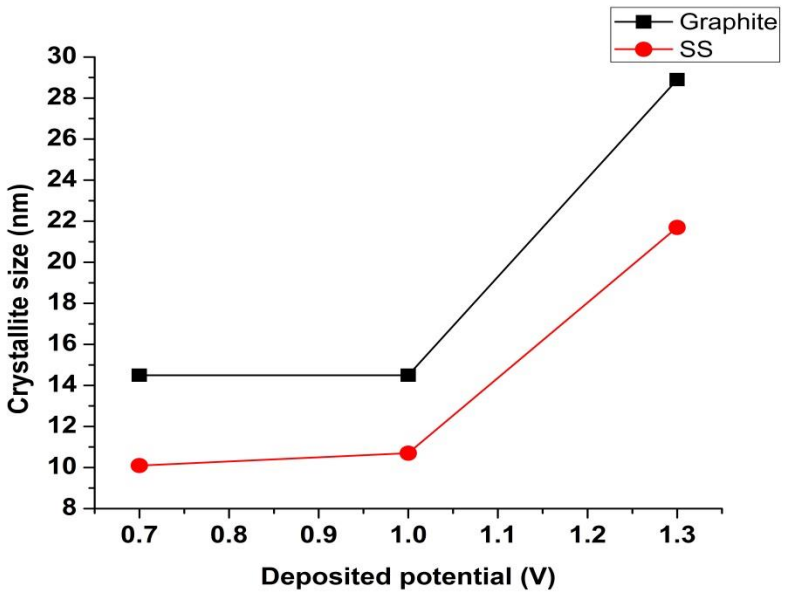


Fig. 4.3: Crystallite size vs Deposition voltage

4.2 Microscopic Analysis

The nucleation and grain growth behavior of the Cu thin films were studied. To understand their growth behavior, deposition were carried at two conditions:

1. The deposition voltage is maintained constant and by varying the bath temperature alone.
2. The bath temperature is held constant (25°C) with varying voltage (0.7, 1 and 1.3 V)

The copper sulphate ($CuSO_4$) precursor is dissolved in water making a bath composition of 0.1M $CuSO_4.5H_2O$, 40 g/l H_2SO_4, 1M of Na_2SO_4 and 0.05 cm^2. The purpose of addition of sodium sulphate is to improve the conductivity of the bath. The Cu^{2+} ions are attracted when the negative voltage is applied to the working electrode. In order to minimize the surface energy the atoms has to travel towards the electrode leading to the formation of the nuclei. Further, concentration of copper sulphate plays a major role in nucleation mechanism. Nominal copper concentration 2.4 gm in 100 ml (0.1M) enables better nucleation at the high temperatures. Fig. 4.4 shows the SEM images of the Cu deposits on graphite for scheme-1. From Fig. 4.4(a) it has been observed that the deposits at 0.35 V (10°C) consist of individual spherical nanosized particles. On further increase of the temperature to 18°C, the copper ions further apart from the electrode travels towards leading to the formation of nuclei.

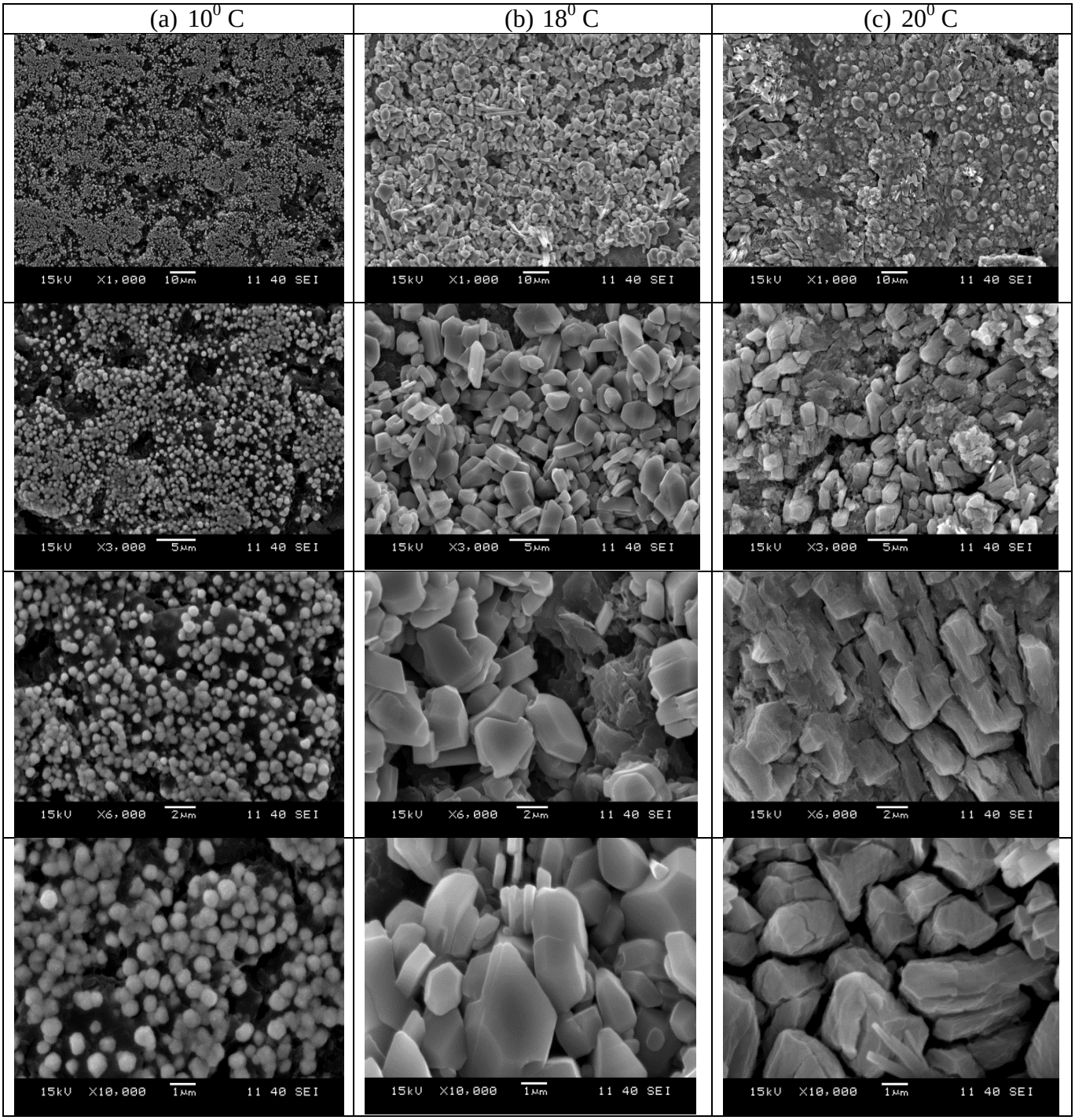


Fig. 4.4: SEM of Cu thin films on graphite deposited at various temperature with potential of -0.35V at different magnifications.

The small nuclei acts as the nucleation site and the nucleation is followed by grain growth, which can be clearly seen from the SEM image Fig. 4.4(b) and distinct grain boundary

formations were observed for Cu thin films deposited at 20°C in Fig.4.4(c). Temperature is an influential parameter for tuning the morphology of the thin films. Earlier Darko Grujicic, Batric Pesic [64] carried a systematic study on nucleation formation of copper nanoparticles at low and high copper sulphate concentrations. The free standing copper ions permeate through the liquid boundary film and gets reduce to form small nuclei. At high concentration, the nucleation is more favorable due to the presence of excess copper ions, similar to the obtained SEM results. Fig. 4.5 shows the schematic representation of the same.

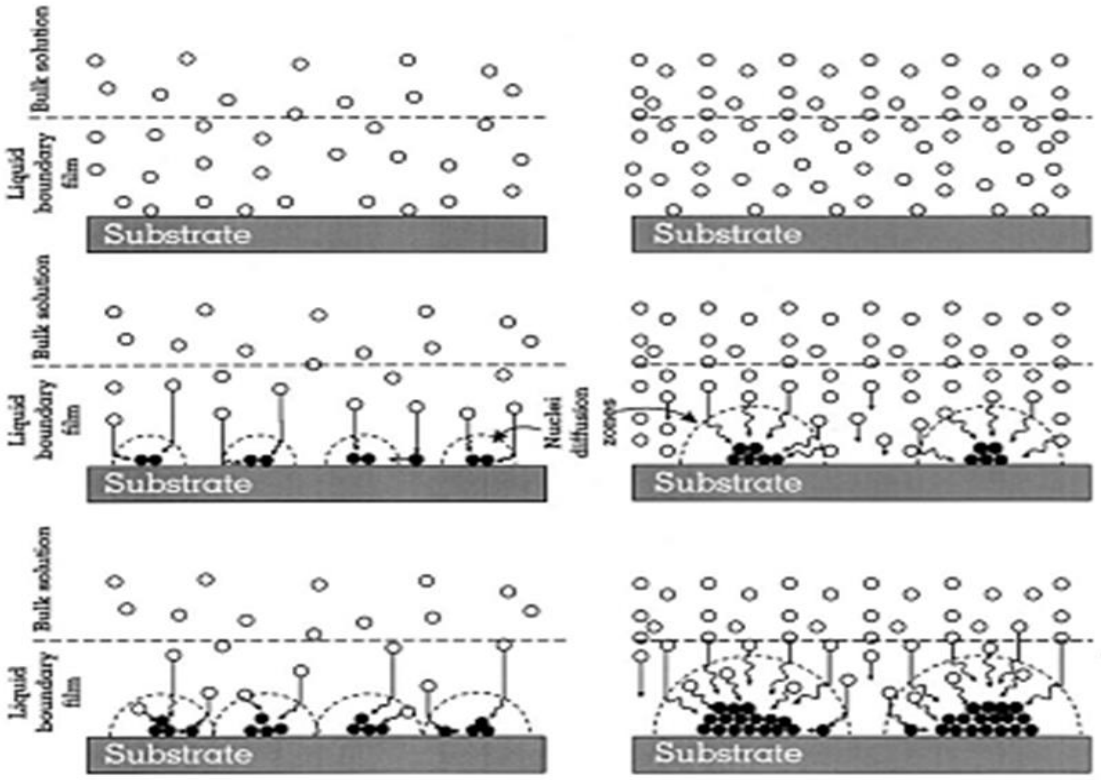


Fig. 4.5: Schematic presentation for (a) lower and (b) higher concentration of metal ions during deposition [64].

Since better grain growth was obtained at 20°C for scheme 1, a temperature of 25°C was chosen for scheme-2. Fig.4.6 shows the FESEM image of the Cu thin films deposited at various voltages. The effect on nucleation and grain growth of the Cu deposits at various voltages can be clearly visualized by the FESEM image. At low voltage 0.7V, fine sized particles are obtained which started to nucleate leading to grain growth. Poor coverage was

observed for 1 V and are merely individual particles was obtained (Fig. 4.6(a)). For higher voltage, at 1.3V, better nucleation and grain growth was observed providing better substrate coverage. The tradeoff between the quickness of the nucleation and grain growth is the key role for microstructure evolution. For 1.3 V, the nucleation and grain growth must have taken fast due to the high deposition voltage, leading to the formation of such high agglomerated patterned thin film FESEM with extremely high coverage (Fig. 4.6(c)).

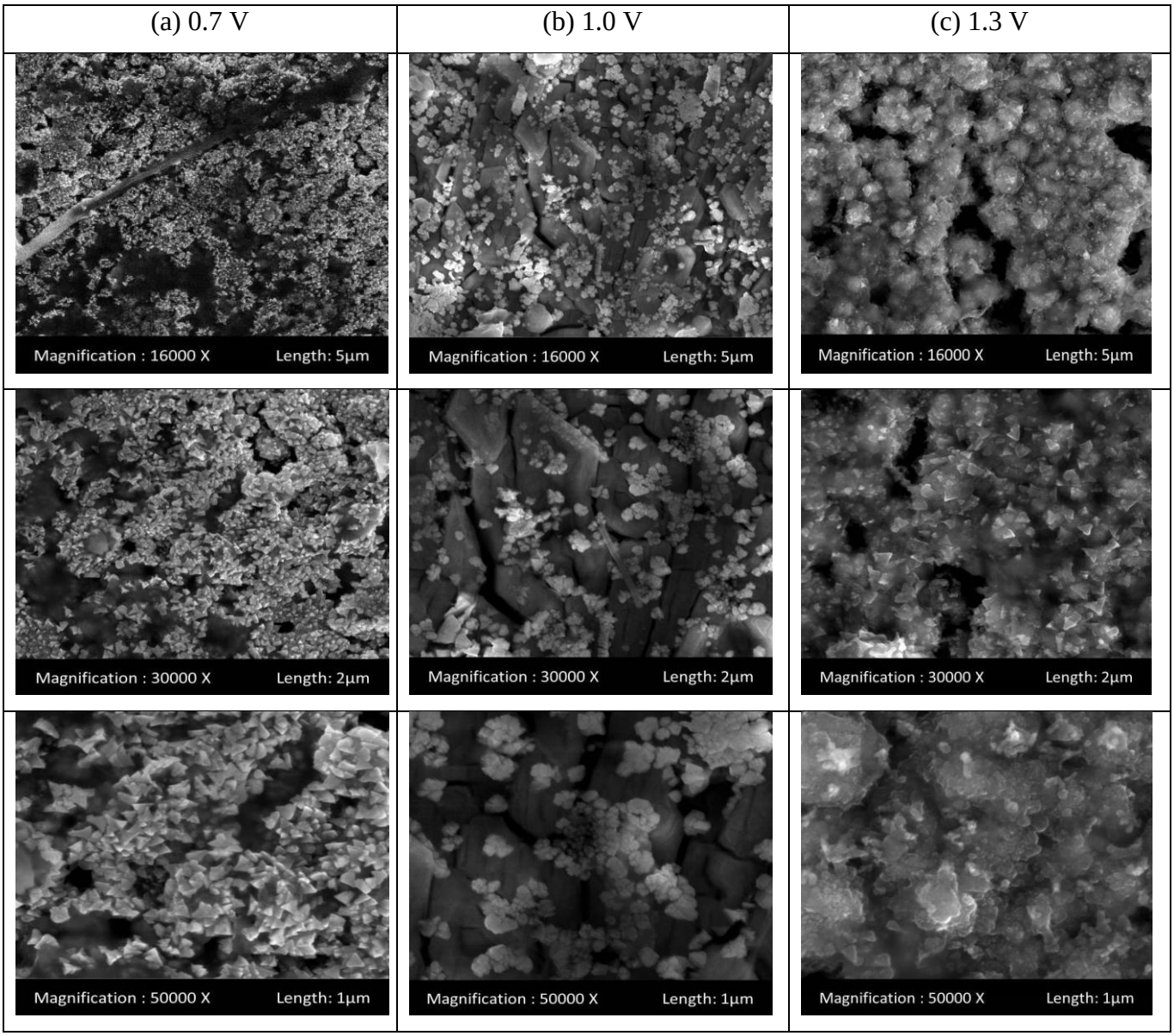


Fig. 4.6: FESEM of Cu thin films on graphite deposited at various potential -0.7V,-1.0V and -1.3V at ambient temperatures (25°C), at various magnifications.

In case of films synthesized on SS similar trends were observed in terms of temperature and potential variation.

4.3 Stylus Surface Profiler Study

The stored energy in a thin film after deposition is known as residual stress. The microstructure of the thin film depends on the extent of interaction existing between the substrate and the thin film coating. This parameter is essential for obtaining a better coating on any substrate. The residual stress components namely the tensile and compressive stress studies of the thin films are studied using stylus Profilometer. The change in radius of curvature of the substrate (*Rs*) and the coated area (*Rc*), along with the thickness data of thin film and substrate are used and calculated by Stoney formula. The radius of curvature will be either convex or concave, influenced by the attractive and repulsive nature of the substrate with the thin film. The convex & concave will give compressive (negative) and tensile stress (positive) respectively. Thin film properties and mechanical performance are affected by residual stress. Different field caused by residual stress which was build up around lattice imperfections and dislocations, superimpose with in a grain. It was basically occurred at thermal cycling, interface coherency and change in deposition parameters. [65-67].For the required thin film deposition it was important to know the source of stresses and to control them. Residual stress can be expressed as

$$\sigma = \sigma_{th} + \sigma_{i} + \sigma_{e}$$

where,

σ_{th} =Thermal stress is due to the difference in thermal coefficient of substrate and deposited films,

σ_{i} = Intrinsic stress is due to the intrinsic factors like lattice mismatch,presence of impurities etc.

σ_{e} = Extrinsic stress is due to the external factors.

Wafer curvature method is used to measure residual stress. Whether as the film thickness is thinner than the substrate, then the residual stress of the film is calculated by using the Stoney's equation [68-69] which is shown below,

$$\sigma_f = \frac{1}{6}\left(\frac{1}{R_2} - \frac{1}{R_1}\right)\frac{E_s t_s^2}{(1-\upsilon_s)}\left[1 - \frac{t_f}{t_s}\right]$$

where, E_s is that the Young's modulus, υ_s is that the Poisson's ratio of the substrate. R_1 and R_2 are substrate's radii of curvature before and after film deposition respectively. t_s is the thickness of the substrate and t_f is the thickness of the film.Fig. 4.7 and 4.8 show examples of one such calculation obtained by the Dektak software.

Fig. 4.7: Tensile as well as compressive stress generated during the film growth observed from Dektak software of Stylus surface profilometer.

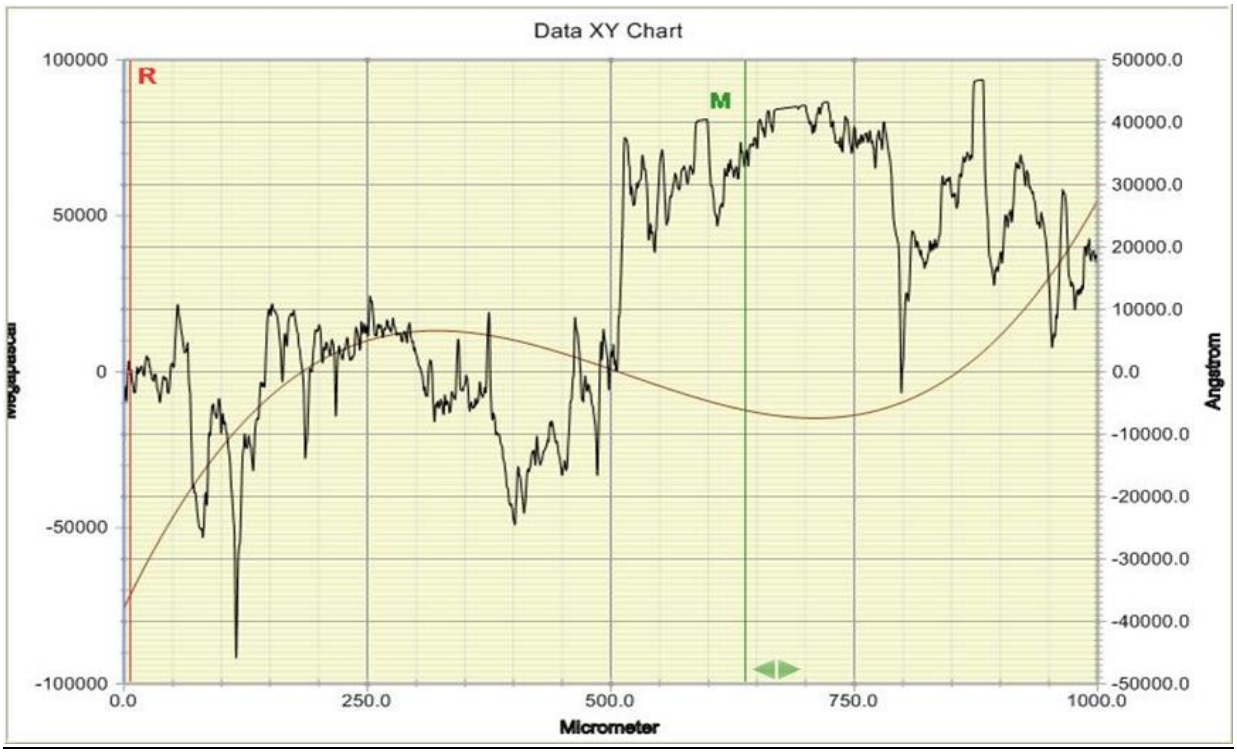


Fig. 4.8: Tensile as well as compressive stress generated during the film growth observed from Dektak software of Stylus surface profilometer.

Fig. 4.9 shows the plot of deposition voltage Vs the residual stress components. An Intriguing results can be seen. It is well known that the substrate crystal structure affects the stress of the thin film. For the SS, the tensile component is high compared to the compressive stress for all the deposition voltage and temperature. It emphasizes the attractive nature of the substrate and thin film coating leading to a concave surface and upward shaped bending profile (the interface is being pulled in) [70]. Moderate deposition voltage (1 V) shows higher tensile stress than the others for both the bath temperatures (0.7 V and 1.3 V at 15° and 25°C). The number of Cu monolayers deposited on the substrate influences the stress component. When the monolayers increase, the impact of the residual stress becomes negligible. A tensile component value varied between 17 to 35 GPa for all the Cu thin films on SS substrate. The compressive stress was found to be very low with a maximum of 7 GPa and 4 GPa as minimal. The temperature effect on the stress can be clearly seen from the plot. To obtain a Cu thin film of minimal tensile stress when coated on SS substrate, the suitable parameters are low deposition voltage at ambient temperature.

The compressive stress component is higher than the tensile, leading to a convex surface and downward shaped bending profile (the interface is being pulled out) due to the repulsive nature between the graphite substrate and the Cu thin film [70]. The compressive stress variation of thin films carried at 15°C was very similar to that of tensile behavior of Cu on SS substrate. The reason stated for the Cu on SS suits well for the graphite samples also. Whereas the deposition carried at 25°C, the compressive stress showed a descending nature. The stated stress values are not uniform all over the substrate. The radius of curvature of the substrate is found to be the position dependent. A very high stress values were also obtained in some position (data not mentioned) which may be due to the vast deviation of the radii of curvature of the substrate. The higher voltage and ambient bath temperature gave Cu thin films of low compressive stress.

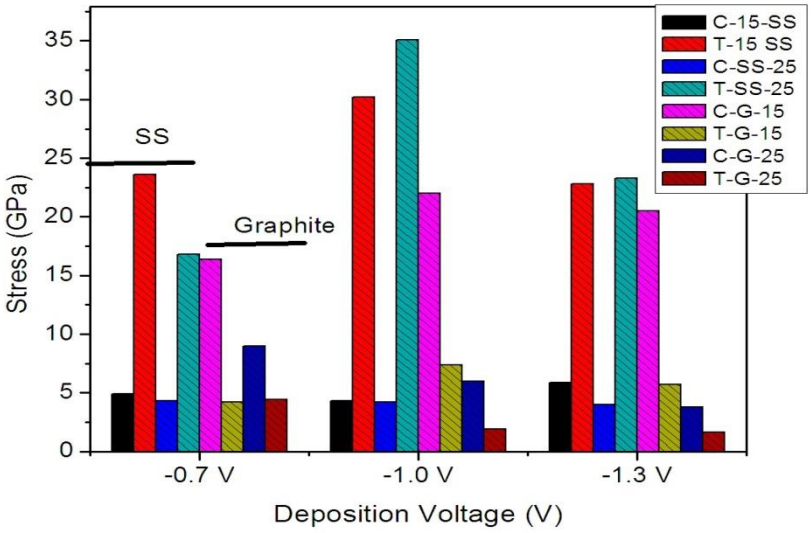


Fig.4.9: Bar graph between Stress (compressive and tensile) vs Deposition Voltage of graphite and SS substrate at 15°C and 25°C.

From the Profilometer scan, thickness and roughness of the deposited films were also calculated. Fig. 4.10 shows the thickness and roughness calculation screen for deposition made on SS substrate. Similarly Fig. 4.11 shows the same on graphite substrate. At the interface point of substrate-film. From the height difference the thickness was calculated. Like these as examples other films were also characterized and the summery of those are tabulated in Table 4.2.

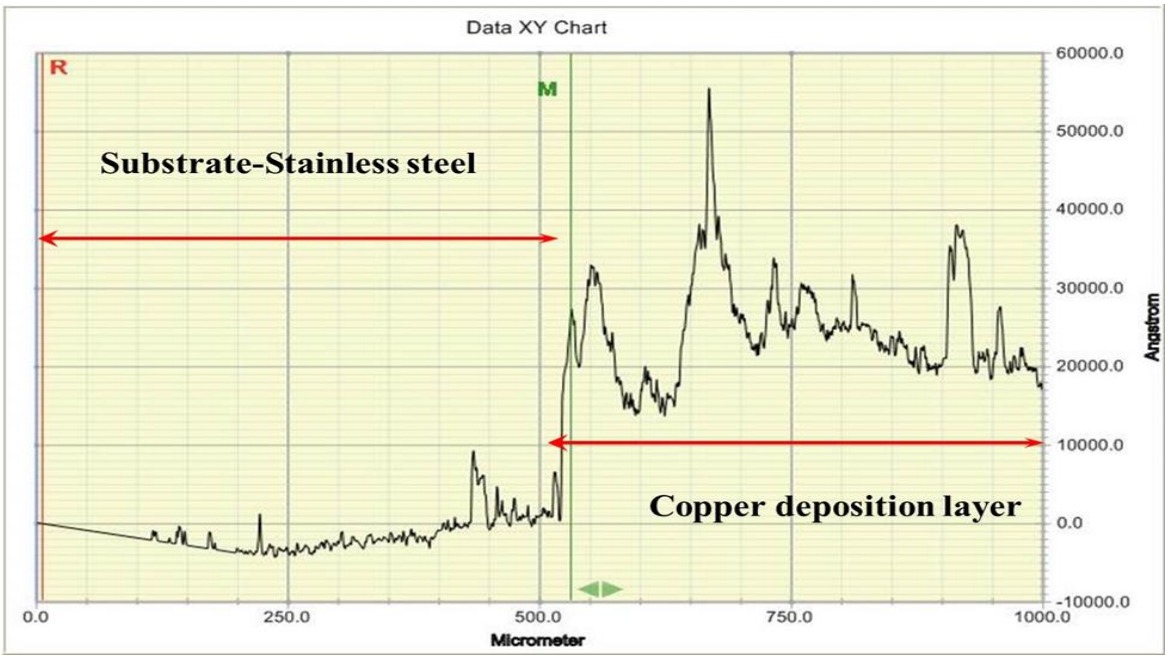


Fig. 4.10: Film thickness of electrodeposited copper observed from the Dektak offline software of Stylus surface profilometer.

Fig. 4.11: Showing the film thickness of electrodeposited copper observed from the Dektak offline software of Stylus surface Profilometer.

Table 4.2: Roughness and thickness values of the Cu film obtained from deposition conditions.

Substrate	Temperature (^oC)	Potential (V)	Roughness (nm)	Thickness (μm)
SS	25	-0.7 V	651.6	2.400
		-1.0 V	232.2	1.185
		-1.3 V	334.7	1.795
	15	-0.7 V	804.2	1.916
		-1.0 V	202.3	1.472
		-1.3 V	520.5	1.446
Graphite	25	-0.7 V	1154.7	3.564
		-1.0 V	842.2	3.689
		-1.3 V	1083.5	3.272
	15	-0.7 V	498.5	3.060
		-1.0 V	560.1	2.491
		-1.3 V	460.6	1.734

From Table 4.2 it can be observed that in general with increase in deposition potential (in negative side) the film thickness decreases. This trend can be observed in both type of substrates. Moreover, deposition synthesized at higher temperature brings more thickness. This can be attributed towards higher ionic mobility at higher temperature leading to higher growth rate of the film. When the effect of substrate on film thickness was considered, it was observed that the thickness is more in case of graphite as substrate. This can be correlated with the fact that residual stress is favorable in case of graphite substrate compared to SS substrate (Fig. 4.9). Better stress condition increases the film thickness easily.

In case of roughness it was observed that irrespective of substrate and temperature, intermediate potential value brings lowest roughness in general. At lower potential the growth is less and only islands are formed (Fig. 4.6) and thus the roughness is more at lower potential. In case of highest potential the growth is high leading to irregular random increase of the island which also brings higher roughness. Thus, the optimum condition of low roughness was observed in case of intermediate voltage only. This can also be observed from the table that at higher temperature the film roughness increases and it happens due to higher growth rate of the film.

CHAPTER 5

CONCLUSIONS

5. Conclusions

To conclude, Cu thin films were deposited successful on ferritic stainless steel and graphite substrate. The crystal structure influence of the substrate on the thin film morphology, Stress evolution and crystallinity were studied and compared. Following conclusions can be drawn from the present study:

1. With increase of deposition bias the crystallite size increases in case of both graphite and stainless steel substrate. Low deposition voltage is more advantageous when deposition was on SS substrate.
2. The effect of varying temperature and deposition voltage on nucleation and growth was studied using SEM and FESEM image analysis. For constant deposition voltage (0.35V), the deposits at 10°C consist of individual spherical nanosized particles. On further increase of the temperature to 18°C, the copper ions further apart from the electrode travels towards leading to the formation of nuclei. The small nuclei act as the nucleation site and the nucleation is followed by grain growth. Distinct grain boundary formations were observed for Cu thin films deposited at 20°C.
3. At low voltage (0.7V), fine sized particles are obtained which started to nucleate leading to grain growth. Poor coverage was observed for 1 V and are merely individual particles was obtained. For higher voltage, at 1.3V, better nucleation and grain growth was observed providing better substrate coverage.The quickness of the nucleation and grain growth is the key role for microstructure evolution which is found to be temperature and deposition voltage dependent.
4. In present study, the tensile stress is more in all the case of Cu thin films deposited on the SS substrate compared to graphite as substrate. For graphite, the compressive stress component is observed to be predominant. Irrespective of the temperature and the deposition voltage, compressive stress is considerably larger than the tensile stress. This is due to the repulsive nature of the graphite surface to the Copper atoms inducing compressive stress in excess.

5. A negligible compressive stress resembles the attractive nature of SS to the Cu thin film. This interesting result helps in identifying the substrate compatibility for any coating. The residual stress values are found to be affected by the bath temperature as well as thickness.Increase in film thickness reduces the effect of residual stress. This may be due to stress relaxation and reduced effect of residual stress when the coating layers increases. From this analysis it can be observed that the deposition on graphite may be better if the film property is concerned for less residual stress.
6. Roughness values of the deposited film were found to be minimum in intermediate deposition potential due to optimum nucleation and growth combination.

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